

Carbonate Fuel Cell Matrix Strengthening

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INTRODUCTION

The present baseline electrolyte matrix is a porous ceramic powder bed impregnated with alkali carbonate electrolyte. The matrix provides both ionic conduction and gas sealing. During fuel cell stack operation, the matrix may experience both mechanical and thermal changes. Different mechanical characteristics of active and wet seal areas can generate stress. A thermal stress is also generated by nonuniform temperature distribution. The matrix is exposed to thermal stresses during heating, cooling as well as operation. A carbonate fuel cell generally may experience several such cycles between 650°C and room temperature during its 40,000h life. Strengthening of the matrix may be beneficial for enhancing robustness of the carbonate fuel cell for withstanding thermo-mechanical stresses. So far, systematic investigation of the various materials and reinforcement approaches for carbonate fuel cell matrix strengthening has not been carried out. Therefore, this DOE/SBIR sponsored study was focused to develop and systematically optimize cost-effective approaches to further strengthen the carbonate fuel cell matrices.

OBJECTIVES AND APPROACH

The objective of this study is to develop a carbonate fuel cell matrix to impart ruggedness to the power plant system for thermo-mechanical stresses. Approaches commonly used for strengthening ceramics were evaluated. Various strengtheners were screened, in terms of strengthening potential and stability. The matrix fabrication process were developed as necessary to incorporate the strengtheners. Matrix samples were evaluated in out-of-cell testing to determine microstructure and mechanical properties. Lab-scale single-cell testing was performed to determine ruggedness to thermo-mechanical stresses. The most promising approach will be evaluated in stack tests.

PROJECT DESCRIPTION

The major efforts in this SBIR research include: 1) developing and selecting strengtheners and matrix fabrication techniques, 2) out-of-cell evaluation, 3) in-cell testing, and 4) stack testing. The project is described below.

Preliminary development of strengtheners and matrix casting process modifications were carried out in Phase I. The directions to develop stable strengtheners and definition of the processes for implementing the potential strengtheners were identified. A single-cell test was performed to demonstrate the benefit of a proposed strengthening approach.

In Phase II, screening of various commercial and experimental strengtheners was first carried out. The strengtheners thus screened (based on strength and stability considerations) were then be incorporated into the matrix (at different contents) for out-of-cell and in-cell evaluation. Advanced cost-effective dispersion methods were investigated. The matrix fabrication process was adjusted as necessary to uniformly disperse the selected strengtheners.

Green, debindered as well as carbonate-filled samples were evaluated in out-of-cell metallographic, bending, indentation and peeling tests to determine microstructure and mechanical properties. Weibull statistical analysis was conducted to determine matrix reliability. In-cell tests is conducted in 250cm² single cells. The matrix gas sealing efficiency is frequently measured during the in-cell testing. Acoustic emission technique was used to identify test conditions which may result in matrix performance change. Post-test analysis performed to determine chemical stability of the strengtheners and to verify/understand the mechanisms of matrix strengthening used chemical methods, SEM/EDAX, TEM, and XRD.

As a final product, the most promising matrix will be selected for evaluation in 10-cell 9,000-cm² full-area subscale stack tests. FCMC, ERC's manufacturing subsidiary, will perform the matrix scale-up activity for stack use. The optimized strengthening approach will be recommended for commercialization.

RESULTS

Strengtheners Selection, Matrix Fabrication and Out-of-Cell Evaluation

The considerations for material selection included strengthening potential, stability and cost. Ceramic particulates and fibers have been proposed for reinforcing carbonate fuel cell matrix [1]. Metallic wire screen has also been proposed [2]. As reported previously [3], several candidate materials, experimental as well as commercial, were evaluated in detail in corrosion/out-of-cell testing. Significant test results have been accumulated. So far, three reinforcement approaches (designated as A, B and C) received most detailed evaluation. Approach A meets the cost and stability goals but not the strength goal. Approach B enhances strength and toughness more than the Approach A. However, stability and cost goals were not met.

The innovative Approach C appears to have the highest potential to achieve all the goals. This approach requires only low-cost additives to enhance the strength during both stack conditioning and operation. During the conditioning, the binder in the matrix is removed. Without such additives, the binderless matrix is only a packed ceramic powder bed, very weak in structure. Therefore, cracking can easily form due to the mechanical or thermal stress. Such cracks may propagate during operation to form thru-cracks, reducing matrix sealing efficiency. Strengthening of the debindered matrix is highly desired to prevent the initiation of such cracks. One major advantage of this approach over the approaches A and B is the much higher strength enhancement of the binderless matrix. In addition, the Approach C also has the same potential of enhancing both strength and toughness of the electrolyte-filled matrix as the Approach B. Several potential low-cost additives for the Approach C are being considered.

Matrices incorporating the candidate strengtheners were fabricated using processes modified from ERC's baseline. The process variables (viscosity, slurry formulation, doctor blade geometry, etc.) were adjusted so that a uniform dispersion of the strengthener phase was successfully achieved. All the fabricated green matrices had adequate strength, pliability and thickness variation for cell and stack use. Scaling up to 10 gallon size slurry manufacturing capacity with uniform distribution of the additives was also successful. Order of magnitude reduction of manufacturing time has been demonstrated by using an advanced manufacturing method. Slurry formulation was successfully modified for cost reduction while maintaining the desired slurry and green tape properties. Tensile and peeling testing were extensively used during organic reformulation to optimize green tape strength, flexibility and laminability.

Tensile, indentation and bending tests were performed on small-size debindered as well as carbonate-filled matrix samples to determine mechanical properties. SEM, TEM and XRD analyses of the tested samples verified the strengthening mechanism as reported in the literature. At least five-fold improvement in room-temperature bending strength was achieved for the Approach C, compared with approaches A and B. The cost comparison also showed that the Approach C provides the most cost-effective strengthening (Figure 1). Therefore, the Approach C was focused in single-cell evaluation.

In-Cell Evaluation

Matrices incorporating the advanced reinforcement approach were evaluated in 250cm² single cells. No difficulties were encountered in implementing these advanced matrices in the cells. So far, about thirty cells incorporating the Approach C have been tested. Figure 2 shows that the BOL (beginning-of-life) matrix sealing efficiency is significantly improved compared to the baseline matrix, using the advanced approach. The primary information recorded is the change in matrix sealing efficiency during the cooldown-restart cycling. These cell tests have shown significant improvements in maintaining matrix seal efficiency during such cycling, as shown in Figure 3. High back pressure capability was also demonstrated (Figure 4). Based on these encouraging results, the Approach C is selected for further optimization and stack evaluation.

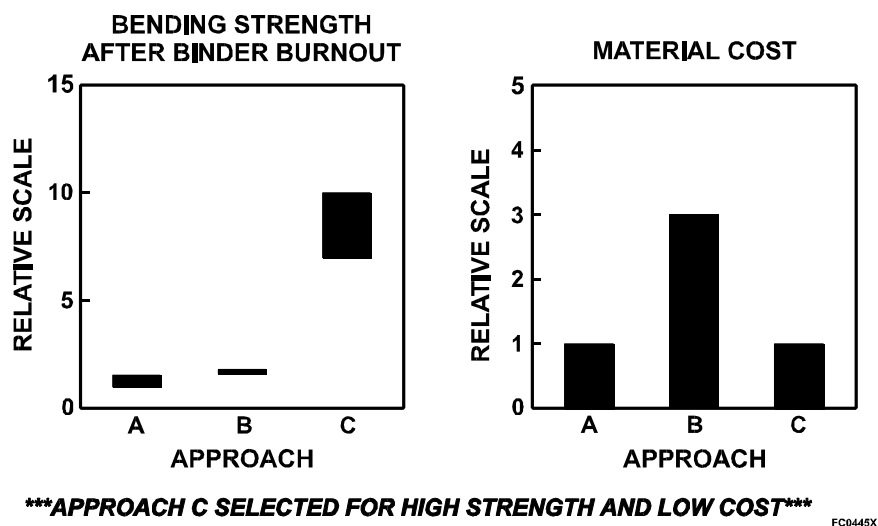


Figure 1. COMPARISON OF MATRIX STRENGTH AND COST:
Approach C Provides the Most Cost-Effective Strengthening.

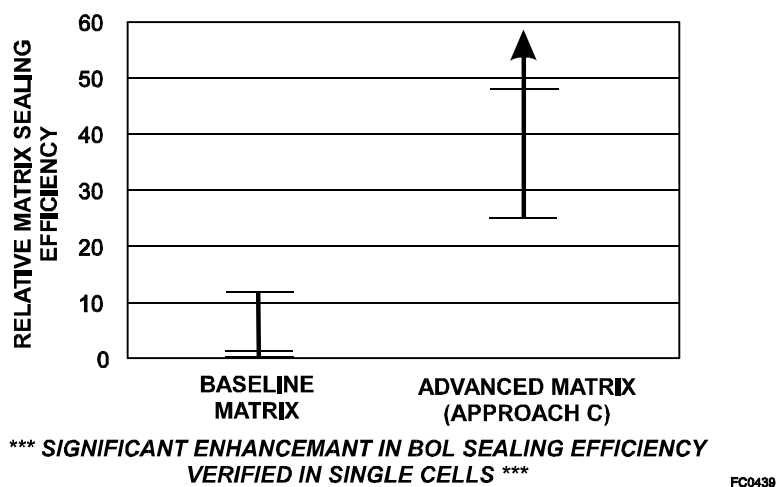


Figure 2. COMPARISON OF MATRIX SEALING EFFICIENCY:
Significant Enhancement in BOL Gas Sealing Efficiency by Advanced Matrix Strengthening Approach C Verified in Single Cells.

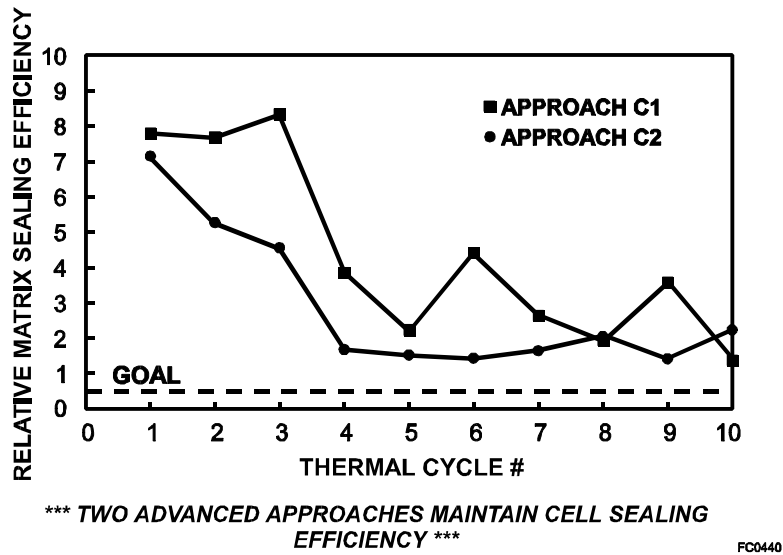


Figure 3. EFFECT OF THERMAL CHANGE ON SEALING EFFICIENCY:
Advanced Strengthening Approach C Maintain Cell Sealing Efficiency

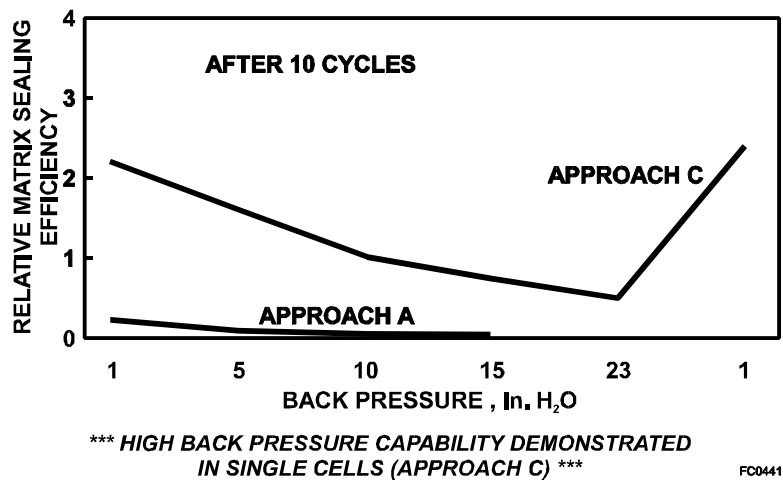


Figure 4. EFFECT OF BACK PRESSURE ON SEALING EFFICIENCY:
High Back Pressure Capability with Advanced Strengthening Approach C
Demonstrated in Single Cells.

CONCLUSIONS

Several promising strengthening concepts were evaluated. An innovative approach C provided the most cost-effective strengthening and gas sealing.

Matrix fabrication technique was successfully adjusted for incorporating the advanced strengtheners. The scale up was also successful.

APPLICATION/BENEFITS

This research is for developing a unique carbonate fuel cell matrix to impart ruggedness to the power systems for thermo-mechanical stresses, particularly from cool down-restart cycle of a power plant. Matrix ruggedness impacts matrix gas sealing efficiency, carbonate fuel cell useful life, conversion efficiency, and the decay rate. The present generation carbonate system projects to a competitive cost of electricity for utility applications, assuming a 5-year useful life. Improvement of system performance as promised by the robust matrix being developed here is expected to significantly increase the competitive position of this unique product by further prolonging useful life as well as improving efficiency. Therefore, this research will promote to a speedy commercialization of carbonate fuel cell technology.

FUTURE ACTIVITIES

Based on the out-of-cell and in-cell test results available, a strengthening approach was identified as the most promising approach. Additional out-of-cell/in-cell testing to optimize the approach in terms strengthening and cost will be conducted. Stack evaluation and incorporation of the matrix in the commercial design will follow.

ACKNOWLEDGEMENT

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